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RESEARCH ARTICLE

APPLICATION OF BIOREMEDIATION TECHNOLOGIES IN THE REMEDIATION OF AGRICULTURAL LAND IN THE AREA OF ZENICA

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Abstract

The paper presents a study of the effects of soil bioremediation of contaminated soils by sowing Corn (Zea mays L.) and alfalfa (Medicago sativa L.) at three locations in the area of Zenica(Gradišće, Stranjani, and Šerići) in the spring of 2018. From March to September, soil samples were gathered to determine the concentration of the following heavy metalsiron (Fe), manganese (Mn), zinc (Zn), nickel (Ni), lead (Pb), vanadium (V), molybdenum (Mo), cadmium (Cd), chromium (Cr), copper (Cu) and cobalt (Co). The initial soil analysis shows that the soil's average concentrations of manganese, nickel, vanadium, cadmium, and molybdenum exceed the permitted limit value. The values of average phytoaccumulation coefficients indicate that alfalfa removes heavy metals in the soil more successfully for iron (0.0346 mg/kg), nickel (0.0732 mg/kg), lead (0.0892 mg/kg), vanadium (0.1152 mg/kg), molybdenum (0.072 mg/kg) and chromium (0.2182 mg/kg). The highest averagetransfer coefficient valueswere achieved for zinc (3.4157 mg/kg) and copper (4.1129 mg/kg) when corn was used. Both plants reached the same levelof cobalt accumulation (2.5 mg/kg).

Introduction:-

For several decades, the areas of Zenica were under the influence of high emissions of dust containing heavy metals, sulfur dioxide, and other pollutants emitted from metallurgical and thermal power plants. The content of heavy metals in the soil has increased compared to the natural state and the limit values prescribed by the Regulation [1], which is a consequence of its anthropogenic redistribution during the operation of the integral production in ironworks Zenica.

Research conducted over five years period by the Federal Institute for Agropedology in the area of the Municipality of Zenica [2] concludes that the soil has an elevated content of nickel, manganese, lead, cadmium, zinc, and copper.The last research carried out by the Institute Kemal Kapetanović - Laboratory for Environmental Pollution Measurement [3] shows that the soil around Ironworks Zenica is contaminated with higher values of heavy metals than the prescribed limit values in the Regulation[1], namely manganese (6 to 8 times), nickel (5 times), cadmium (4 to 6 times) and zinc (2 times).All this indicates the riskiness of crop production, as well as the riskiness of the health of people who use crops grown in the area of Zenica. Therefore, it is necessary to take measures to remediate agricultural land to ensure agricultural production and protect people's health.

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One of the available options for removing toxic substances from the soil is bioremediation, which stands out as one of the best methods due to the lesser level of environmental disturbance and it costs less. The study aims to look into the bioremediation technology of agricultural land across three different locations in Zenica, each representing different types of soil. Therefore, the presence of heavy metals in the soil and dry plant material will be monitored, as well as determining the effectiveness of the application of certain plant species that have good potential for the remediation of contaminated land parcels.

Bioremediation is a natural process by which polluting substances are biologically transformed into less toxic or non-toxic compounds or are completely broken down into carbon dioxide and water. Phytoremediation is a method of remediation, renewal, and land clearing using plants. The best results are achieved in removing heavy metals. The principle of phytoremediation is that the plants absorb heavy metals from the soil solution through their roots and accumulate them in the roots and other parts of the plant.

The intensity of uptake of heavy metals and their accumulation in plants is primarily influenced by the concentration of heavy metals in the external environment, especially the concentration of dissolved (active) forms of metals, the pH value of the soil, the content of carbonates and organic matter in the soil, the degree of soil humidity and other edaphic factors.The genetic specificity of certain plant species and the participation of metals in biochemical reactions during their uptake and transport have a significant influence on metal uptake [4].

The physical and chemical properties of the soil have a great influence on the accumulation and retention of heavy metals in the soil, as well as their mobility and translocation.Soils with a high content of organic matter, carbonates, and phosphates bind heavy metals in inaccessible forms, which are difficult to transfer to the plant [5].

Material and Methods:-

This research was conducted across three locations within the Zenica area, which were chosen, based on a cyclical circle system at varying distances ranging from 2.78 to 16.4 km from the primary industrial sources of dust and heavy metal emissions. These sources predominantly included metallurgical and thermal energy plants in Zenica (Table 1.).A graphical representation of sampling locations is shown in Figure 1.

Table 1:- Distance of the locality of industrial emission sources.

N.o.	**Location**	**Distance (km)**	**Geographical latitude**	**Geographical longitude**	**Altitude**
1.	Gradišće	2,78	44^0 14’13” N	17^0 52’8” E	528 m
2.	Stranjani	4,88	44^0 13’14” N	17^0 50’54” E	565 m
3.	Šerići	16,4	44^0 21’30” N	17^0 48’23” E	809 m

Soil sampling was conducted on representative plots with an area of 300 m^2 in each of the designated locations (Table 1.). Samples were collected before and after sowing and harvesting plant crops to evaluate the initial and final concentrations of heavy metals in the soil. The presence of the amount of 11 heavy metals (Fe, Mn, Zn, Ni, Pb, V, Mo, Cd, Cr, Cu, Co) and the pH value in the soil and in dry plant material was determined by chemical analyses.

An average sample (about 2 kg) was collected from several (10-20) individual samples taken with a shovel and a hand tool.The samples were taken mainly from agricultural land used as natural or artificial grassland, from a depth of 25 cm.The procedure by which the soil is prepared for chemical analysis includes the operations of drying, shredding, sieving, and packing.

In this experiment, air drying (air-dry samples) was used, and it was done in a ventilated and special room outside the reach of the laboratory or some other gases and dust. Samples brought from the field are placed on a larger piece of harder paper or cardboard and flattened by hand to a thickness of 1 to 2 cm.First, foreign matter (roots, stones, worms, small animals, etc.) was removed from the soil samples. The sample was spread thinly on clean paper and gradually air-dried without direct sunlight. After a few days of occasional stirring, the sample was air-dried. After drying, samples were crushed and sieved through a sieve with openings of diameter 1 - 2 mm. The sieved samples were packed in paper bags and then transported to the chemical laboratory for further analysis.

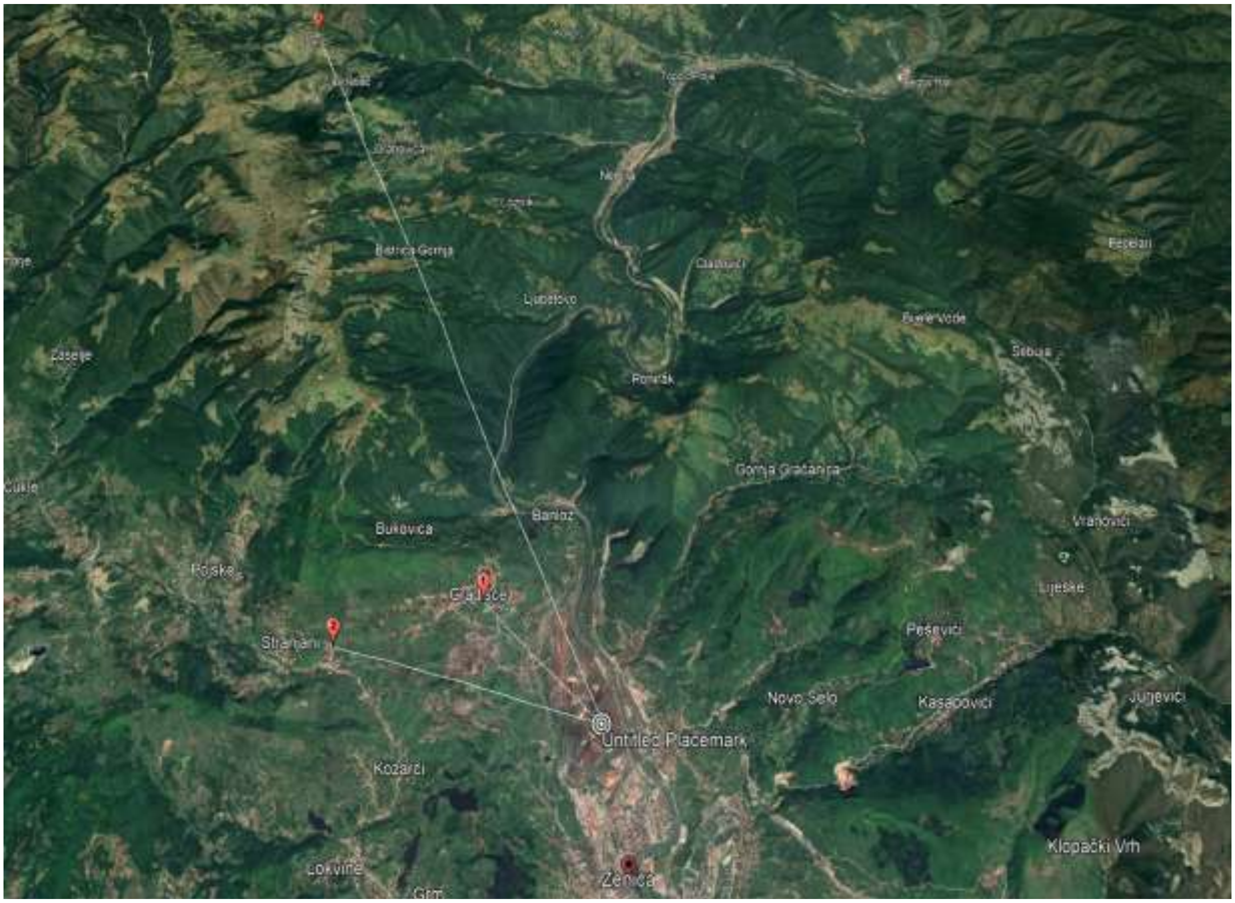

Figure 1:- Overview map showing soil sampling locations.

Standard methodologies were used for planting corn (Zea mays L.) and alfalfa (Medicago sativa L.). At the end of the growing season, plants were sampled manually, including above-ground parts (stems with leaves) and roots. Only healthy and undamaged plant specimens (large, medium, and small) were collected to obtain a representative sample. If the sampled parts had a light dust cover, they were gently brushed. Any present stones, plant residues, etc., were removed from the sample. Before drying, root samples were washed with distilled water to remove soil residues and other deposited impurities. In the laboratory, the above-ground parts of corn and alfalfa plants with roots were chopped into smaller pieces, spread thinly on clean paper, and left to gradually air-dry for 15-20 days without direct sunlight. Soil sample preparation for chemical analysis was performed in the laboratory by quartering each sample to obtain 100 g samples. Heavy metal content was determined using the atomic absorption spectrophotometry method (PERKIN ELMER Analytical Methods for Atomic Absorption Spectrometry).

The most suitable way to represent the uptake of metals from soil into plants is through the translocation coefficient of heavy metals (KP) or the phytoaccumulation coefficient of metal translocation from soil to plants. The translocation coefficient is defined as the ratio of concentrations of heavy metals in the plant to those in the soil.

$$KP = \frac{heavy\ metal\ content\ in\ the\ plant\ (mg/kg)}{heavy\ metal\ content\ in\ the\ soil\ (mg/kg)}$$

The permissible limits of heavy metals (GV) depending on soil texture are defined by the Regulation [1] (Tables 2, 3, and 4). The soil texture of the investigated locations is powdery-clayey. The permissible limits for manganese and iron according to H. Resulović (Tables 2, 3, and 4) are taken from the Report [2]. These soil permissible limits apply to soils with acidic reactions. For alkaline and carbonate soils, these values may be increased by 25%.

Results and Discussion:-

The natural content of metals in the soil is as follows: for lead, it's 0.1-20 mg/kg, for cadmium 0.1-1 mg/kg, for iron 3.2%, for zinc 3-50 mg/kg, for nickel 40 mg/kg, for chromium 100 mg/kg, and manganese 200-1,000 mg/kg.

Upon reviewing the analyses of heavy metal concentrations from the initial and final analyses in Gradišće (Table 2.), it was noted that the manganese, nickel, lead, vanadium, molybdenum, cadmium, and chromium values increased according to the regulations [1] regarding the natural state of metals in the soil. By conducting the final soil analysis, after the removal of corn and alfalfa, there was a reduction in the quantities of nickel, vanadium, molybdenum, and cadmium. The average pH value in H_2O is 7.6 (weakly alkaline), and the pH in KCl is 7.0 (neutral reaction).

Table 2:- Initial and final soil analysis in the Gradišće location.

Parameter (mg/kg)	Initial analysis	Finalanalysis G-Soil-K1	Final analysis G-Soil-L1	GV (mg/kg)
Fe	42.000 (4,2%)	45.890 (4,589 %)	43.590 (4,359 %)	5%
Mn	**1417**	**1400**	**1440**	1.000.
Zn	29	10	10	150
Ni	**111**	**80**	**90**	40
Pb	59	**90**	**70**	80
V	**104**	**50**	<1	40
Mo	**20**	<1	<1	15
Cd	**1,4**	<0,1	<0,1	1,0
Cr	78	**90**	**100**	80
Cu	29	50	60	65
Co	<1	<1	<1	45
pH u H_20	7,7	7,4	7,6	-
pH u KCl	7,0	6,6	7,0	-

Note: The shaded numbers indicate exceeding the threshold values.
G-Soil-K1 - sample from the parcel where corn was used
G-Soil-L1 - sample from the parcel where alfalfa was used

Initial and final soil analysis at the Stranjanilocationis given in Table 3. Data from table 3 shows that the average concentrations of manganese, nickel, vanadium, molybdenum, and cadmium at the Stranjanilocation exceed the prescribed threshold value according to Regulation [1]. After the final soil analysis, the values of nickel, vanadium, molybdenum, and cadmium were reduced. The average pH value in H_2O is 7.3 (slightly alkaline), and the pH in KCl is 6.4 (slightly acidic).

Table 3:- Initial and final soil analysis at the Stranjanilocation.

Parameter (mg/kg)	Initial analysis	Final analysis S-Soil-K1	Final analysis S-Soil-L1	GV (mg/kg)
Fe	34.633 (3,4633%)	35.500 (3,55 %)	36.100 (3,61 %)	5%
Mn	**1667**	**1630**	**1630**	1.000.
Zn	21	20	20	150
Ni	**66**	**60**	**70**	40
Pb	25	50	10	80
V	**67**	**60**	<1	40
Mo	**24**	<1	<1	15
Cd	**1,36**	<0,1	<0,1	1,0
Cr	41	70	80	80
Cu	31	40	30	65
Co	<1	<1	<1	45
pH u H_20	7,6	7,2	7,1	-
pH u KCl	6,8	6,4	6,5	-

Note: Shaded numbers indicate exceeding the threshold values.
S-Soil-K1 - sample from the parcel where corn was used
S-Soil-L1 - sample from the parcel where alfalfa was used

At the Šerići location (Table 3), prescribed values for manganese, nickel, vanadium, and copper in the soil have been exceeded. The concentrations of manganese and cadmium are three times higher than the permitted values according to Regulation [1]. Conduction bioremediation using corn the values of nickel, vanadium, and cadmiumhave been reduced. The average pH value in H2O is 6.0 (slightly acidic), and the pH in KCl is 5.3 (moderately acidic).

Table 4:- Initial and finalsoil analysis at the Šerići site.

Parameter (mg/kg)	**Initial analysis**	**Final analysis Š-Soil-K1**	**Final analysis Š-Soil-L1**	**GV(mg/kg)**
Fe	22700 (2,27%)	24980 (2,498 %)	26980 (2,698 %)	5%
Mn	**3063**	**3000**	**2730**	1.000.
Zn	19	20	20	150
Ni	**46**	40	**60**	40
Pb	23	20	70	80
V	**44**	<1	20	40
Mo	5	<1	<1	15
Cd	**3**	<0,1	<0,1	1,0
Cr	16	30	40	80
Cu	49	**80**	**80**	65
Co	<1	<1	<1	45
pH u H_20	6,2	5,9	5,8	-
pH u KCl	5,6	5,1	5,3	-

Note: Shaded numbers indicate exceeding the threshold values.
Š-Soil-K1 - sample from the parcel where corn was used
Š-Soil-L1 - sample from the parcel where alfalfa was used

In the final soil analyses at the given locations, an increase in the values of certain metals (nickel, chromium, copper, manganese, and lead) has been noticed compared to the results of the initial analysis (Tables 2, 3, and 4).The reason for increased values of certain elements could be an increased amount of sediment dust and heavy metals in it [3], concerning the direction and speed of the prevailing winds [6].

The most productive plants in creating a large amount of biomass from cereals are all varieties of corn, wheat, and barley. The usual bioaccumulation factor for corn is for Zn 1-2 and for Cd, Cu, and Pb 0.01-0.05 [7]. Other authors state that this factor is different for different contaminated substrates and amounts 0.82 for Zn; 0.33 for Cd; 1.08 for Cu and 0.07 for Pb [8].
According to data presented in Table 5. it is clear that corn achieves the best average values of the metal transfer coefficient for copper (4.1129 mg/kg), zinc (3.4157 mg/kg), and cobalt (2.5 mg/kg). Comparing the results between the locations, the highest value of the transfer coefficient when using corn was registered at the location of Šerići for nickel (0.0243 mg/kg), vanadium (0.1136 mg/kg), molybdenum (0.0125 mg/kg), iron (0.0110 mg/kg), (chromium 0.3125 mg/kg) and lead (0.0029 mg/kg). Namely, the type of soil prevalent in Šerići is distric brown soil that has relatively high acidity and low carbonate content with an unfavorable ratio of Ca^{2+} ions [4]. In such conditions, heavy metals show increased mobility.This type of soilis represented in the farthest locations from Ironworks Zenica.

Greater phytoextraction of manganese (0.0546 mg/kg) and cadmium (0.01 mg/kg) was achieved at the Gradišće site (Table 5). The soil type in Gradišće is rendzina, which provides a good supply of humus and a high carbonate content with a favorable ratio of Ca^{2+}ions on marls and marly clays [4] of higher soil pH values, thatimmobilizes heavy metals and makes it difficult for plants to absorb them. It is most prevalent in the area closer to the ironworks Zenica, which has certain ecological advantages as it immobilizes heavy metals relatively well and has good buffering properties. The intensity of metal binding in the soil and the stability of the bonds decreases with the decrease in the pH value, the content of organic matter, and carbonate in the soil. Under such conditions, some of the heavy metals form easily soluble compounds, which are available to plants.

Average values of the phytoaccumulation coefficient of cornare given in the following table.

Table 5:- Average values of the phytoaccumulation coefficient of corn.

CORN Parameters	**Locations**			**Average (mg/kg)**
	Gradišće	**Stranjani**	**Šerići**	
Fe	0,0041	0,0055	0,0110	0,0067
Mn	0,0546	0,0314	0,0350	0,040
Zn	0,0034	6,428	3,8157	3,4157
Ni	0,0009	0,0015	0,0243	0,0089
Pb	0,0016	0,0026	0,0029	0,0023
V	0,0961	0,0373	0,1136	0,0823
Mo	0,005	0,0041	0,0125	0,0072
Cd	0,01	0,005	0,0033	0,0061
Cr	0,0320	0,1219	0,3125	0,1554
Cu	0,2586	11,774	0,3061	4,1129
Co	2,5	2,5	2,5	2,5

Data from the Table 5. shows that the highest plant accumulation values for zinc (6,428 mg/kg) and copper (11,774 mg/kg) were achieved at the Stranjani location. The indicated location is a eutrophic brown soil with slightly acidic to acidic pH value and lower carbonate content.

Experiments with alfalfa (Medicago sativa L.) in hydroponic systems showed that this plant can absorb up to 85% of Cd from the dilution during 21 days. Plants from the true grass family represent one of the most important phytoremediators of heavy metals and organic compounds because, in addition to being able to remove large amounts of various pollutants, they can also create a large amount of biomass in one season.

The highest average values of alfalfa phytoaccumulation coefficient were achieved for cobalt (2.5 mg/kg) and zinc (1.450 mg/kg) at the Šerići location and for copper (0.431 mg/kg) at Gradišće location (Table 6).

Table 6:- Average values of the phytoaccumulation coefficient of alfalfa (Medicago sativa L.).

ALFALFA Parameters	**Locations**			**Average (mg/kg)**
	Gradišće	**Stranjani**	**Šerići**	
Fe	0,0288	0,0277	0,0471	0,0346
Mn	0,0423	0,0284	0,0538	0,0415
Zn	0,0034	0,0047	4,3421	1,450
Ni	0,0009	0,0015	0,2173	0,0732
Pb	0,0016	0,2631	0,0029	0,0892
V	0,1201	0,1119	0,1136	0,1152
Mo	0,005	0,0041	0,0125	0,072
Cd	0,01	0,005	0,0033	0,0061
Cr	0,0641	0,1219	0,4687	0,2182
Cu	0,431	0,3225	0,3061	0,3532
Co	2,5	2,5	2,5	2,5

Based on the data from Tables 5 and 6, it is noticeable that alfalfa showed a higher average value of the phytoaccumulation coefficient for the manganese, nickel, lead, vanadium, molybdenum, and chromium,which exceeded the proscribed limit values (Tables 3 and 4). Both plants show the same transfer coefficient values for cadmium and cobalt. It is evident from the transfer coefficient that copper, zinc, and cobalt have high mobility in the soil and are easily absorbedby plants.

Conclusion:-

Soil initial analysis shows that average concentrations of manganese, nickel, vanadium, and cadmium are higher than the permissible limit for all examined areas in Zenica. Elevated concentrations of molybdenum in the soil were registered at two locations: Gradišće and Stranjani. Comparing the results of average heavy metal concentration values from the initial soil analysis with the results of the final analysis after plant removal, a reduction in concentrations of zinc, nickel, molybdenum, cadmium, and vanadium was noticed. Alfalfa as a phytoremediator, has a greater ability to extract iron, nickel, lead, vanadium, molybdenum, and chromium from the soil compared to corn at various sites in the Zenica area. Concerning the concentration of metals in soil, several vegetation seasons will be necessaryto reduce concentrations of certain heavy metals below proscribed limits. Due to the high achieved transfer coefficient for zinc, copper, and cobalt, it is best to use corn for phytoextraction of these heavy metals. In future phytoremediationprojects, monitoring of soil and total sediment dust should be performedsimultaneously with the planting of corn and alfalfa to obtain the relationship between metal phytoaccumulationas well as the relationship between heavy metals in the soil and sediment dust.

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